

Chapter 6

- 6-1.** (a) The *standard error of the mean* is the standard deviation of the mean and is given by the standard deviation of the data set divided by the square root of the number of measurements.
- (b) The *coefficient of variation* is the percent relative standard deviation or $(s / \bar{x}) \times 100\%$.
- (c) The *variance* is the square of the standard deviation.
- (d) *Significant figures* are all the digits in a number that are known with certainty plus the first uncertain digit.
- 6-2.** (a) The term *parameter* refers to quantities such as the mean and standard deviation of a population or distribution of data. The term *statistic* refers to an estimate of a parameter that is made from a sample of data.
- (b) The population mean is the true mean for the population of data. The sample mean is the arithmetic average of a limited sample drawn from the population.
- (c) *Random errors* result from uncontrolled variables in an experiment while *systematic errors* are those that can be ascribed to a particular cause and can usually be determined.
- (d) *Accuracy* represents the agreement between an experimentally measured value and the true or accepted value. *Precision* describes the agreement among measurements that have been performed in exactly the same way.
- 6-3.** (a) The *sample standard deviation s* is the standard deviation of a sample drawn from the population. It is given by $s = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}}$, where \bar{x} is the sample mean.

The *population standard deviation* σ is the standard deviation of an entire population

given by $\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \mu)^2}{N}}$, where μ is the population mean.

(b) In statistics, a sample is a small set of replicate measurements. In chemistry, a sample is a portion of a material that is taken for analysis.

- 6-4.** The standard error of a mean, s_m , is the standard deviation of the set of data, s , divided by the square root of the number of data in the set, i.e. $s_m = s / \sqrt{N}$. The standard error of the mean s_m is lower than the standard deviation of the data points in a set s because a set of data made up of means will have less spread than a set of data made up of data points.

In the equations for s_m , the denominator (\sqrt{N}) always has a value greater than 1 so that s_m will always be less than s .

- 6-5.** Since the probability that a result lies between -1σ and $+1\sigma$ is 0.683, the probability that a result will lie between 0 and $+1\sigma$ will be half this value or 0.342. The probability that a result will lie between $+1\sigma$ and $+2\sigma$ will be half the difference between the probability of the result being between -2σ and $+2\sigma$, and -1σ and $+1\sigma$, or $\frac{1}{2}(0.954 - 0.683) = 0.136$.

- 6-6.** Since the probability that a result lies between -2σ and $+2\sigma$ is 0.954, the probability that a result will lie outside this range is $(1 - 0.954) = 0.046$. The probability that a result will be more negative than -2σ will be half this value, or 0.023.

- 6-7.** Listing the data from Set A in order of increasing value:

x_i	x_i^2
9.5	90.25
8.5	72.25
9.1	82.81
9.3	86.49
9.1	82.81
$\Sigma x_i = 45.5$	$\Sigma x_i^2 = 414.61$

(a) mean: $\bar{x} = 45.5/5 = 9.1$

(b) median = 9.1

(c) spread: $w = 9.5 - 8.5 = 1.0$

(d) standard deviation: $s = \sqrt{\frac{414.61 - (45.5)^2/5}{5-1}} = 0.37$

(e) coefficient of variation: $CV = (0.37/9.1) \times 100\% = 4.1\%$

Results for Sets A through F, obtained in a similar way, are given in the following table.

	A	B	C	D	E	F
\bar{x}	9.1	55.29	0.650	5.1	20.61	0.958
median	9.1	55.32	0.653	5.0	20.64	0.954
w	1.0	0.15	0.108	1.5	0.14	0.049
s	0.37	0.08	0.056	0.6	0.07	0.02
CV, %	4.1	0.14	8.5	12.2	0.32	2.1

6-8. For Set A, $E = 9.1 - 9.0 = 0.1$

$$E_r = (0.1/9.0) \times 1000 \text{ ppt} = 11.1 \text{ ppt}$$

$$\text{Set B, } E = -0.040 \quad E_r = -0.7 \text{ ppt}$$

$$\text{Set C } E = 0.0195 \quad E_r = 31 \text{ ppt}$$

$$\text{Set D } E = -0.34 \quad E_r = -63 \text{ ppt}$$

$$\text{Set E } E = 0.03 \quad E_r = 1.3 \text{ ppt}$$

$$\text{Set F } E = -0.007 \quad E_r = -6.8 \text{ ppt}$$

6-9. (a) $s_y = \sqrt{(0.03)^2 + (0.001)^2 + (0.001)^2} = 0.030$

$$CV = (0.03/2.082) \times 100\% = -1.4\%$$

$$y = -2.08(\pm 0.03)$$

(b) $s_y = \sqrt{(0.04)^2 + (0.0001)^2 + (0.08)^2} = 0.089$

$$CV = (0.089/19.1637) \times 100\% = 0.46\%$$

$$y = 19.16(\pm 0.09)$$

(c) $\frac{s_y}{y} = \sqrt{\left(\frac{0.3}{29.2}\right)^2 + \left(\frac{0.02 \times 10^{-17}}{2.034 \times 10^{-17}}\right)^2} = 0.01422$

$$CV = (0.0142) \times 100\% = 1.42\%$$

$$s_y = (0.0142) \times (5.93928 \times 10^{-16}) = 0.08446 \times 10^{-16}$$

$$y = 5.94(\pm 0.08) \times 10^{-16}$$

(d) $\frac{s_y}{y} = \sqrt{\left(\frac{1}{326}\right)^2 + \left(\frac{2}{740}\right)^2 + \left(\frac{0.006}{1.964}\right)^2} = 0.00510$

$$CV = (0.00510) \times 100\% = 0.510\%$$

$$s_y = (0.00510) \times (122830.9572) = 626$$

$$y = 1.228(\pm 0.006) \times 10^5$$

(e) $s_{num} = \sqrt{(6)^2 + (3)^2} = 6.71 \quad y_{num} = 187 - 89 = 98$

$$s_{den} = \sqrt{(1)^2 + (8)^2} = 8.06 \quad y_{den} = 1240 + 57 = 1297$$

$$\frac{s_y}{y} = \sqrt{\left(\frac{6.71}{98}\right)^2 + \left(\frac{8.06}{1297}\right)^2} = 0.0688$$

$$CV = (0.0688) \times 100\% = 6.88\%$$

$$s_y = (0.0688) \times (0.075559) = 0.00520$$

$$y = 7.6(\pm 0.5) \times 10^{-2}$$

(f) $\frac{s_y}{y} = \sqrt{\left(\frac{0.01}{3.56}\right)^2 + \left(\frac{3}{522}\right)^2} = 0.006397$

$$CV = (0.006397) \times 100\% = 0.6397\%$$

$$s_y = (0.006397) \times (6.81992 \times 10^{-3}) = 4.36 \times 10^{-5}$$

$$y = 6.82(\pm 0.04) \times 10^{-3}$$

6-10. (a) $s_y = \sqrt{(0.02 \times 10^{-8})^2 + (0.2 \times 10^{-9})^2} = 2.83 \times 10^{-10}$

$$y = 1.02 \times 10^{-8} - 3.54 \times 10^{-9} = 6.66 \times 10^{-9}$$

$$CV = \frac{2.83 \times 10^{-10}}{6.66 \times 10^{-9}} \times 100\% = 4.25\%$$

$$y = 6.7 \pm 0.3 \times 10^{-9}$$

(b) $s_y = \sqrt{(0.08)^2 + (0.06)^2 + (0.004)^2} = 0.10$

$$y = 90.31 - 89.32 + 0.200 = 1.190$$

$$CV = \frac{0.10}{1.190} \times 100\% = 8.41\%$$

$$y = 1.2(\pm 0.1)$$

(c) $\frac{s_y}{y} = \sqrt{\left(\frac{0.0005}{0.0040}\right)^2 + \left(\frac{0.02}{10.28}\right)^2 + \left(\frac{1}{347}\right)^2} = 0.1250$

$$CV = (0.1250) \times 100\% = 12.5\%$$

$$y = 0.0040 \times 10.28 \times 347 = 14.27$$

$$s_y = (0.125) \times (14.27) = 1.78$$

$$y = 14(\pm 2)$$

$$(d) \quad \frac{s_y}{y} = \sqrt{\left(\frac{0.03 \times 10^{-14}}{223 \times 10^{-14}} \right)^2 + \left(\frac{0.04 \times 10^{-16}}{1.47 \times 10^{-16}} \right)^2} = 0.0272$$

$$CV = (0.027) \times 100\% = 2.7\%$$

$$y = 1.63 \times 10^{-14} / 1.03 \times 10^{-16} = 1.517 \times 10^4$$

$$s_y = (0.0272) \times (1.517 \times 10^4) = 0.0413 \times 10^4$$

$$y = 1.52(\pm 0.04) \times 10^4$$

$$(e) \quad \frac{s_y}{y} = \sqrt{\left(\frac{1}{100} \right)^2 + \left(\frac{1}{2} \right)^2} = 0.500$$

$$CV = (0.500) \times 100\% = 50.0\%$$

$$y = 100 / 2 = 50.0$$

$$s_y = (0.500) \times (50.0) = 25$$

$$y = 50(\pm 25)$$

$$(f) \quad s_{\text{num}} = \sqrt{(0.02 \times 10^{-2})^2 + (0.06 \times 10^{-3})^2} = 2.09 \times 10^{-4}$$

$$\text{num} = 0.0149 - 0.00497 = 0.00993$$

$$s_{\text{den}} = \sqrt{(0.7)^2 + (0.08)^2} = 0.704$$

$$\text{den} = 27.1 + 8.99 = 36.09$$

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.000209}{0.00993}\right)^2 + \left(\frac{0.704}{36.09}\right)^2} = 0.0287$$

$$CV = (0.0287) \times 100\% = 2.87\%$$

$$y = 0.00993/36.09 = 2.751 \times 10^{-4}$$

$$s_y = (0.0287) \times (2.751 \times 10^{-4}) = 7.899 \times 10^{-6}$$

$$y = 2.75(\pm 0.08) \times 10^{-4}$$

6-11. (a) $y = \log(2.00 \times 10^{-4}) = -3.6989$ $s_y = \frac{(0.434)(0.03 \times 10^{-4})}{(2.00 \times 10^{-4})} = 6.51 \times 10^{-3}$

$$y = -3.699 \pm 0.0065$$

$$CV = (0.0065/3.699) \times 100\% = 0.18\%$$

(b) As in part (a): $y = 37.645 \pm 0.001$

$$CV = 0.003\%$$

(c) $y = \text{antilog}(1.200) = 15.849$ $\frac{s_y}{y} = (2.303)(0.003) = 0.0069$

$$s_y = (0.0069)(15.849) = 0.11 \quad y = 15.8 \pm 0.1$$

$$CV = (0.11/15.8) \times 100\% = 0.69\%$$

(d) As in part (c): $y = 3.5(\pm 0.3) \times 10^{49}$

$$CV = 9.2\%$$

6-12. (a) $y = (4.17 \times 10^{-4})^3 = 7.251 \times 10^{-11}$ $\frac{s_y}{y} = 3 \left(\frac{0.03 \times 10^{-4}}{4.17 \times 10^{-4}} \right) = 0.0216$

$$s_y = (0.0216)(7.251 \times 10^{-11}) = 1.565 \times 10^{-12} \quad y = 7.3(\pm 0.2) \times 10^{-11}$$

$$\text{CV} = (1.565 \times 10^{-12} / 7.251 \times 10^{-11}) \times 100\% = 2.2\%$$

(b) As in part (a): $y = 1.3090(\pm 0.0002)$

$$\text{CV} = 0.02\%$$

6-13. From the equation for the volume of a sphere, we have

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi \left(\frac{d}{2}\right)^3 = \frac{4}{3}\pi \left(\frac{2.15}{2}\right)^3 = 5.20 \text{ cm}^3$$

Hence, we may write

$$\frac{s_V}{V} = 3 \times \frac{s_d}{d} = 3 \times \frac{0.02}{2.15} = 0.0279$$

$$s_V = 5.20 \times 0.0279 = 0.145$$

$$V = 5.2(\pm 0.1) \text{ cm}^3$$

6-14. The mean diameter of the tank is $\bar{d} = \frac{5.2 + 5.7 + 5.3 + 5.5}{4} = 5.425 \text{ m}$ The standard

deviation of the diameter is $s_d = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}} = 0.222$. The standard deviation of the

mean diameter is $s_d / \sqrt{4} = 0.111$.

The mean height of the tank is $\bar{h} = \frac{7.9 + 7.8 + 7.6}{3} = 7.767 \text{ m}$ and $s_h = 0.153$. The

standard deviation of the mean height is $s_h / \sqrt{3} = 0.0883$

The volume of the tank is given by

$$V = h \times \pi \left(\frac{d}{2} \right)^2 = 7.767(\pm 0.0883) \times \pi \times \left(\frac{5.425(\pm 0.111)}{2} \right)^2$$

The error in the 3rd term is given by

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.111}{5.425} \right)^2} = 0.02046 \quad y = \frac{1}{2} (5.425) = 2.7125 \quad s_y = 0.02046 \times 2.7125 = 0.0555$$

$$V = 7.767(\pm 0.0883) \times (3.14159) \times (2.7125(\pm 0.0555))^2$$

$$\frac{s_y}{y} = 2 \left(\frac{0.0555}{2.7125} \right) = 0.0409 \quad y = (2.7125)^2 = 7.358 \quad s_y = (0.0409)(7.358) = 0.301$$

$$V = 7.767(\pm 0.0883) \times (3.14159) \times 7.358(\pm 0.301)$$

Next, we propagate the error in volume by assuming the error in pi is negligible.

$$\frac{s_y}{y} = \sqrt{\left(\frac{0.0883}{7.767} \right)^2 + \left(\frac{0.301}{7.358} \right)^2} = 0.04246 \quad y = 7.767 \times 3.14159 \times 7.358 = 179.5$$

$$s_y = (0.04246)(179.5) = 7.62$$

$$y = 180(\pm 8) \text{ m}^3$$

Converting to liters, we have

$$V = 180(\pm 8) \text{ m}^3 \times \frac{1000L}{m^3} = 1.8(\pm 0.08) \times 10^5 L$$

- 6-15.** Since the titrant volume equals the final buret reading minus the initial buret reading, we can introduce the values given into the equation for %A.

$$\% A = [9.26(\pm 0.03) - 0.19(\pm 0.02)] \times \text{equivalent mass} \times 100/[45.0(\pm 0.2)]$$

Obtaining the value of the first term and the error in the first term

$$s_y = \sqrt{(0.03)^2 + (0.02)^2} = 0.0361 \quad y = 9.26 - 0.19 = 9.07$$

We can now obtain the relative error of the calculation

$$\frac{s_{\%A}}{\%A} = \sqrt{\left(\frac{0.036}{9.07}\right)^2 + \left(\frac{0.2}{45.0}\right)^2} = 0.00596$$

The coefficient of variation is then

$$CV = (0.00596) \times 100\% = 0.596\% \text{ or } 0.6\%$$

- 6-16.** To obtain a CV in S of 1% or less,

$$\frac{s_S}{S} \leq 0.01 = \sqrt{\left(\frac{s_{k'}}{k'}\right)^2 + \left(\frac{s_{e^{-E/kT}}}{e^{-E/kT}}\right)^2}$$

Since k' is a constant, the first term is zero resulting in:

$$0.01 = \frac{s_{e^{-E/kT}}}{e^{-E/kT}} \quad \text{From Table 6-4} \quad \frac{s_{e^{-E/kT}}}{e^{-E/kT}} = s_{-E/kT}$$

$s_{-E/kT}$ can be determined by evaluation of the errors in each of the numbers.

$$\frac{s_{-E/kT}}{-E/kT} = \sqrt{\left(\frac{s_E}{E}\right)^2 + \left(\frac{s_k}{k}\right)^2 + \left(\frac{s_T}{T}\right)^2}$$

Since both E and k have no uncertainty, this equation reduces to:

$$s_{-E/kT} = \left(\frac{s_T}{T}\right) \times \frac{-E}{kT} = \left(\frac{s_T}{6500}\right) \left(\frac{-6.12 \times 10^{-19}}{(1.3807 \times 10^{-23})(6500)}\right) = 0.01$$

Solving for s_T gives:

$$s_T \leq 9.5 \text{ K}$$

- 6-17.** We first calculate the mean transmittance and the standard deviation of the mean.

$$\text{mean T} = \left(\frac{0.213 + 0.216 + 0.208 + 0.214}{4}\right) = 0.2128$$

$$s_T = 0.0034$$

$$(a) \quad c_X = \left(\frac{-\log T}{\varepsilon b} \right) = \frac{-\log(0.2128)}{3312} = 2.029 \times 10^{-4} \text{ M}$$

$$(b) \quad \text{For } -\log T, \quad s_y = (0.434)s_T/T = 0.434 \times (0.0034/0.2128) = 0.00693$$

$$-\log(0.2128) = 0.672$$

$$c_x = \frac{-\log T}{\varepsilon b} = \frac{0.672 \pm 0.00693}{3312 \pm 12}$$

$$\frac{s_{C_x}}{c_x} = \sqrt{\left(\frac{0.00693}{0.672}\right)^2 + \left(\frac{12}{3312}\right)^2} = 0.0109$$

$$s_{C_x} = (0.0109)(2.029 \times 10^{-4}) = 2.22 \times 10^{-6}$$

$$(c) \quad \text{CV} = (2.22 \times 10^{-6}/2.029 \times 10^{-4}) \times 100\% = 1.1\%$$

6-18. (a) and (b)

	A	B	C	D	E	F	G	H	I	J	K	L
1	Problem 6-18											
2												
3	Sample	1	$(x_i - x_{\text{ave}})^2$	2	$(x_i - x_{\text{ave}})^2$	3	$(x_i - x_{\text{ave}})^2$	4	$(x_i - x_{\text{ave}})^2$	5	$(x_i - x_{\text{ave}})^2$	No. Sets
4												
5		6.02	0.0031	7.48	0.0044	3.90	0.0090	4.48	0.0060	5.29	0.0067	5
6		6.04	0.0058	7.47	0.0032	3.96	0.0012	4.65	0.0086	5.13	0.0061	
7		5.88	0.0071	7.29	0.0152	4.16	0.0272	4.68	0.0150	5.14	0.0046	
8		6.06	0.0092			3.96	0.0012	4.42	0.0189	5.28	0.0052	
9		5.82	0.0207							5.20	0.0001	
10												
11	mean	5.964		7.413		3.995		4.558		5.208		Total
12	s	0.107		0.107		0.114		0.127		0.075		
13	N		5		3		4		4		5	21
14	$\Sigma(x_i - x_{\text{ave}})^2$		0.0459		0.0229		0.0387		0.0485		0.0227	0.17864
15												
16	s _{pooled}	0.11										
17												
18	Spreadsheet Documentation											
19												
20	B11=AVERAGE(B5:B9)											
21	B12=STDEV(B5:B9)											
22	C5=(B5-\$B\$11)^2											
23	C13=COUNT(C5:C9)											
24	C14=SUM(C5:C9)											
25	L13=SUM(C13:K13)											
26	L14=SUM(C14:K14)											
27	B16=SQRT(L14/(L13-L5))											

- (c) Pooling the variations in %K from the five samples gives a better estimate of σ because several data sets are used. Thus the pooled standard deviation uses a larger number of data points and can reflect variations that arise because of sample selection and sample preparation.

6-19.

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Problem 6-19												
2													
3	Sample	1	$(x_i - \bar{x}_{ave})^2$	2	$(x_i - \bar{x}_{ave})^2$	3	$(x_i - \bar{x}_{ave})^2$	4	$(x_i - \bar{x}_{ave})^2$	5	$(x_i - \bar{x}_{ave})^2$	6	$(x_i - \bar{x}_{ave})^2$
4													
5		1.02	0.0049	1.13	0.0020	1.12	0.0071	0.77	0.0100	0.73	0.0144	0.73	0.0008
6		0.84	0.0121	1.02	0.0042	1.32	0.0135	0.58	0.0081	0.92	0.0049	0.88	0.0150
7		0.99	0.0016	1.17	0.0072	1.13	0.0055	0.61	0.0036	0.90	0.0025	0.72	0.0014
8				1.02	0.0042	1.20	0.0000	0.72	0.0025			0.70	0.0033
9						1.25	0.0021						
10													
11	mean	0.950		1.085		1.204		0.670		0.850		0.758	
12	s	0.096		0.077		0.084		0.090		0.104		0.083	
13	N		3		4		5		4		3		4
14	$\Sigma(x_i - \bar{x}_{ave})^2$		0.0186		0.0177		0.0281		0.0242		0.0218		0.0205
15													
16	s_{pooled}	0.088								No. Sets	6		
17													
18	Spreadsheet Documentation												
19										N_{Total}	23		
										$\Sigma(x_i - \bar{x}_{ave})^2$	0.1309		
20	B11=AVERAGE(B5:B9)												
21	B12=STDEV(B5:B9)												
22	C5=(B5-\$B\$11)^2												
23	C13=COUNT(C5:C9)												
24	C14=SUM(C5:C9)												
25	K18=SUM(C13:M13)												
26	K19=SUM(C14:M14)												
27	B16=SQRT(K19/(K18-K16))												
28													

- (a) The standard deviations are $s_1 = 0.096$, $s_2 = 0.077$, $s_3 = 0.084$, $s_4 = 0.090$, $s_5 = 0.104$, $s_6 = 0.083$
- (b) $s_{pooled} = 0.088$ or 0.09

6-20.

	A	B	C	D	E	F
1	Problem 6-20					
2						
3	Sample	x_1	x_2	mean	$(x_1 - x_{ave})^2$	$(x_2 - x_{ave})^2$
4	1	2.24	2.27	2.255	0.00022	0.00023
5	2	8.4	8.7	8.55	0.02250	0.02250
6	3	7.6	7.5	7.55	0.00250	0.00250
7	4	11.9	12.6	12.25	0.12250	0.12250
8	5	4.3	4.2	4.25	0.00250	0.00250
9	6	1.07	1.02	1.045	0.00063	0.00062
10	7	14.4	14.8	14.6	0.04000	0.04000
11	8	21.9	21.1	21.5	0.16000	0.16000
12	9	8.8	8.4	8.6	0.04000	0.04000
13						
14	N	18		Total	0.39085	0.39085
15	No. of Sets	9				
16	s_{pooled}	0.29				
17						
18	Spreadsheet Documentation					
19						
20	D4=AVERAGE(B4:C4)					
21	E4=(B4-\$D\$4)^2					
22	F4=(C4-\$D4)^2					
23	B14=COUNT(B4:C12)					
24	E14=SUM(E4:E12)					
25	B16=SQRT((E14+F14)/(B14-B15))					

6-21.

	A	B	C	D	E	F	G	H
1	Problem 6-21							
2								
3	Sample	1	$(x_i - x_{ave})^2$	2	$(x_i - x_{ave})^2$	3	$(x_i - x_{ave})^2$	No. Sets
4								
5		13	0.06	42	2.78	29	5.76	3
6		19	39.06	40	0.11	25	2.56	
7		12	0.56	39	1.78	26	0.36	
8		7	33.06			23	12.96	
9						30	11.56	
10								
11	mean	12.75		40.33		26.60		Total
12	s	4.92		1.53		2.88		
13	N		4		3		5	12
14	$\Sigma(x_i - x_{ave})^2$		72.75		4.67		33.20	110.62
15								
16	s_{pooled}	3.5						
17								
18	Spreadsheet Documentation							
19								
20	B11=AVERAGE(B5:B9)							
21	B12=STDEV(B5:B9)							
22	C5=(B5-\$B\$11)^2							
23	C13=COUNT(C5:C9)							
24	C14=SUM(C5:C9)							
25	H13=SUM(C13:G13)							
26	H14=SUM(C14:G14)							
27	B16=SQRT(H14/(H13-H5))							

6-22.

	Excel value	NIST value
Mean	2.001856000000000	2.001856000000000
SD	0.000429123454003085	0.000429123454003053

The means are the same in both cases. There is some difference, however, in the standard deviations in the last two digits. The differences could arise because of the different algorithms used to calculate the SD and to roundoff errors in the calculations. The first 16 digits are identical.